Transfer Print of Single Layer Graphene to Polymers

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ABSTRACT

A novel approach to the transfer of graphene from Cu foil to polymers has been developed. It relies on differential adhesion between the foil and the polymer against the graphene layer. Thus, when the graphene-polymer adhesive strength is higher than that of the graphene-metal foil, a successful print is achieved. This straightforward approach eliminates damage to the graphene associated with wet chemical transfer techniques, reduces transfer time, and preserves the metal foil substrates.

INTRODUCTION

To make flexible graphene-based electronics a reality, manufacturable techniques for *both* graphene growth and graphene transfer to insulating substrates are needed. Initially, graphene was obtained by micromechanical cleavage of graphite. However, this technique is now considered a needle-in-a-haystack approach with little control over the transferred amount. More recently, numerous graphene growth methods have been developed including thermal graphitization of SiC, reduction of graphene oxide, and chemical vapor deposition (CVD) on transition metals substrates [1].

For applications ranging from flexible electronics to organic photovoltaics, graphene has to be transferred to a plastic surface with limited damage to its electrical, thermal and mechanical properties. Traditionally, the graphene transfer from transition metal foils has involved a polymer mediator (PMMA or PDMS) to keep the graphene film intact while the Cu foil substrate is chemically etched [2]. The latter requires strong acids such as HNO_3, which can produce hydrogen bubbles that ultimately damage the graphene [3, 4]. Aqueous iron chloride ($FeCl_3$) has been explored as a mild alternative to acid etching but in either case, the metal foil etching step requires hazardous chemicals and it is time consuming process[4]. Following etching, the PMMA/graphene stack is floated in deionized water to remove metal etchant residuals. Then, the graphene/PMMA stack is placed onto substrate of interest. The final step involves the dissolution of PMMA in acetone to yield "pristine" graphene on the desired substrate. The detrimental effect of solvent residues on graphene has been recognized. For example, they may cause the graphene to form cracks upon transfer [5].

Recently, alternative approaches to the use of polymer coatings have been explored, notably those involving thermal release tape [6-8]. The exact transfer protocol varies between research groups; however in all cases the metal foils still need to be chemically etched. As an example, the protocol used by Bae et. al. [8] involves placing tape/graphene/Cu stack between two rollers at 0.2 MPa pressure, then the Cu foil is chemically etched. The Gr/tape stack is washed with deionized water, placed on target substrate and heated (90 - 120°C) to remove tape residues. The use of thermal release tape may be an attractive alternative to polymer supports, however the method is still time consuming, it destroys the metal substrate and generates hazardous chemical waste.

In this paper, an alternative approach [9] to conventional graphene transfer methods by *directly* transferring large, uniform areas of graphene grown on copper foil to polystyrene is described. Graphene was grown on Cu foil using a different growth procedure than the one previously described [9]. Electrical properties of the transferred films were evaluated.

METHODOLOGY, RESULTS, AND DISCUSSION

The method of dry graphene transfer to polystyrene relies on three distinct steps as shown in Figure 1. In the first step, graphene was grown via CVD on a Cu foil and separately, the polymer surface was treated to enhance its adhesion to graphene. The latter process involved plasma-based surface activation and the deposition of N-ethylamino-4-azidotetrafluorobenzoate (TFPA-NH_2) linker molecule. In the second step, the TFPA treated polymer surface was placed in contact with graphene covered Cu foil and printed, under heat and force, in standard wafer bonder. In the final step, the polymer substrate with attached graphene was separated from the metal foil. To ensure successful transfer, the adhesion on two interfaces polymer/TFPA and TFPA/graphene has to be higher than the adhesion between graphene and Cu.

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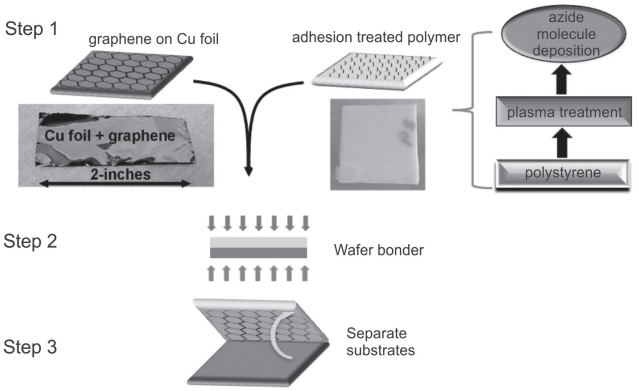

Figure 1: Flow chart of the graphene transfer method: In step 1, graphene film was grown on Cu foil and independently the polymer surface was treated to increase reactivity. In step 2, both substrates were placed in the wafer bonder. In step 3, the substrates were separated and graphene was transferred to the polymer.

The preparation of the polystyrene surface employed a carbon dioxide plasma treatment to create chemical functionality and the subsequent coupling of N-ethylamino-4-azidotetrafluorobenzoate molecule (TFPA) molecules to that surface (Figure 2). Plasma treatment of polystyrene in CO_2 environment generated a combination of hydroxyl and carboxyl functionalities. TFPA was attached to polystyrene on the basis of hydrogen bonding (PS H). The plasma treated polymers were simply dip coated in 4 mM TFPA solution for two hours.

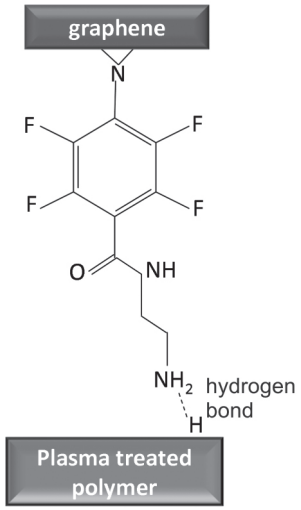

Figure 2: Schematic of hydrogen bond attachment (PS H) between the amine groups of the TFPA and the hydroxyls and carboxyl groups of the plasma treated polystyrene surface.

After the dip coating, the samples were extensively rinsed and sonicated for 10 minutes in methanol and then dried with nitrogen. The prepared substrates were then pressed against graphene on Cu foil and heated for 30 minutes. The azide group which was inactive during TFPA attachment to polymers is heat activated and a covalent amide bond between the graphene and the TFPA is formed. Finally, the Cu foil was peeled off to produce polymer surfaces with the transferred graphene film. No additional cleaning of the surfaces was necessary.

Efficiency of graphene transfer was determined by analyzing both the polymer substrate and the Cu foil employing Raman spectroscopy and electrical measurements. As shown in Figures 3 and 4, graphene was transferred to the polymer as evidenced by the appearance of the graphene specific 2D peak in the Raman data on the TFPA treated polystyrene. Optical images and the Raman spectra of the Cu foil before and after print (Figure 4) also suggests that graphene was removed from the foil. Based on the optical images graphene grains clearly visible on the Cu foil before print are almost diminished after print. Additionally, as shown in Figure 4 graphene signature peaks G and 2D disappeared after transfer.

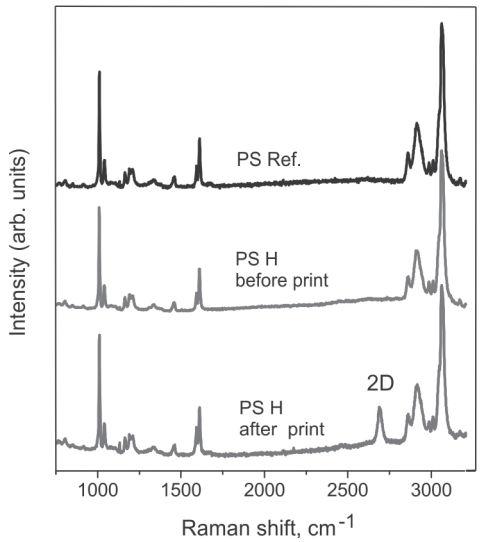

Figure 3: Raman spectra of polystyrene before and after print. The 2D pea appearance after printing is indicative of graphene.

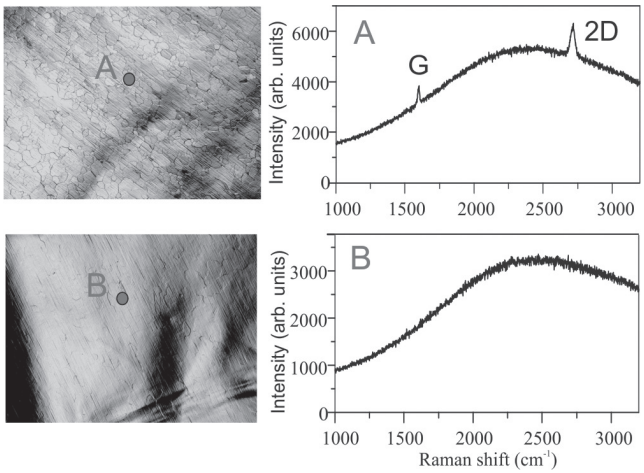

Figure 4: Analysis of Cu foil before and after transfer. The absence of both G and 2D peaks after print indicates that graphene was removed.

The electrical conductivity, carrier densities, mobilities and sheet resistance of the polymer films before and after transfer were determined by Hall measurements using copper pressure clips in a van der Pauw configuration over areas of 0.5 x 0.5 mm^2. The carrier densities on the polymer surface were 4 x 10^{12} cm^{-2} after print. Mobility and the sheet resistence after print were 1000 cm^2/Vs and 2 kΩ/sq respectively. These values are similar to the values previously published by our group[9] and on par or better than those reported for graphene transferred to SiO_2/Si from Cu foils [10,11], suggesting the developed transfer method provides a promising route for graphene transfer to organics.

CONCLUSION

We have demonstrated a unique dry approach for graphene transfer from copper foil to polystyrene based on enhanced adhesion using an azide-containing linker molecule. The Cu foil was not chemically etched and thus it can be reused for future graphene growth. The dry transferred graphene monolayer was uniform and of high quality as signified by low sheet resistance (2 kΩ/sq), high carrier densities (4 x 10^{12} cm^{-2}) and good mobilities (1000 cm^2/Vs). In principle, this method can be applied for graphene transfer to wide range organic or inorganic substrates. Similarly, transfer from other metal growth foils should be possible as well.

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